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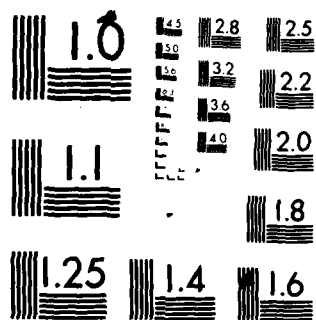
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Synthetic methods for introduction of the pendant high-energy groups nitro and azido into olefinic polymers have been devised. Nitromercuration, base-promoted demercuration and reductive removal of residual mercury yields olefinic polymers with a nitro content of up to 15-20% of theoretical. Azidoiodination followed by dehydroiodination produces azidized olefinic polymers with an azide content of up to 60% of theoretical. Substrates have been poly(cis-1,4-butadiene), CTBN, and HTPB. Samples of nitrated and azidized polymers have been sent to NSWC, White Oak.		

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ANNUAL SUMMARY REPORT

SYNTHESIS AND CHARACTERIZATION OF HIGH ENERGY POLYMERS

INSTITUTION: University of Massachusetts, Amherst

GRANT: ONR N00014-79-C-0265

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## SUMMARY OF PROGRESS

The value of a binder to a propellant system will be significantly enhanced by the introduction of pendant high energy substituents such as azido and nitro groups to the elastomeric backbone. We have developed syntheses for such a purpose with the following substrates: poly(cis-butadiene), PB, carboxy-terminated poly(butadiene-co-acrylonitrile), CTBN and hydroxy-terminated poly(butadiene), HTPB.

For the nitration of diene polymers, the polymer is first treated with  $\text{HgCl}_2$  and  $\text{NaNO}_2$  to give nitromercurated polymers. Our contribution is the finding that phase transfer catalysts allows this reaction to proceed with water-insoluble polymers. We have also optimized the selective formation of nitro groups. The mercury is subsequently removed by treatment with a stoichiometric amount of non-nucleophilic base.

To introduce the azido group, the polymer was first treated with  $\text{ICl}$  and  $\text{NaN}_3$  to give azidoiodinated products. The iodine was subsequently removed with  $t\text{-BuOK}$  in the presence of a crown ether. Good yields were obtained in both reactions.

Samples of nitrated and azidated HTPB have been submitted to Dr. Kurt Mueller at the White Oak Laboratory for evaluation.

## Progress Report

### I. Nitration of Diene Polymers and Copolymers

#### A. Nitromercuration of Carboxy-terminated Butadiene Acrylonitrile Copolymer (CTBN).

CTBN (PBAN) has been nitromercurated under the non-aqueous phase-transfer conditions developed for poly(cis-1,4-butadiene).<sup>1</sup> Results are given in Table I.

Table I

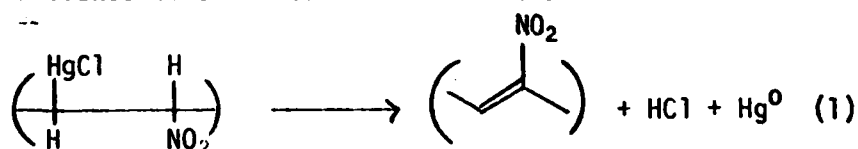
The most important conclusions reached in this study are listed below:

- 1) Nitromercuration beyond ca. the 20% level gives insoluble polymers which are unsuitable in the subsequent demercuration reaction.

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- 2) Only one equivalent of sodium nitrite is necessary.
- 3) The reaction proceeds cleanly and faster at 5 times the polymer concentration used in the previous work on poly-butadiene ( $\overline{MW} \sim 5 \times 10^5$ ).
- 4) Conditions have been found (run 2) to produce a good yield of soluble polymer. Good selectivity for the nitro function at the expense of nitrite ester is apparent in the IR spectrum shown in Figure 1.
- 5) Soluble polymer characteristically exhibits an N/Hg ratio of  $>1$  (nitrogen adjusted for acrylonitrile content of original copolymer) while for insoluble polymer this ratio is  $<1$ .
- 6) Upon drying ( $\text{Na}_2\text{SO}_4$ ) methylene chloride solutions of nitromercurated polymer deposit mercury as a gray solid. Evidence is consistent with the reaction below.

Fig. 1



The atomic ratio N/Hg of the final product  $>1$  and IR bands characteristic of nitroalkene functionality appear at  $1520$  and  $1340 \text{ cm}^{-1}$  (Figure 1).

#### B. Nitromercuration of Hydroxy-terminated Polybutadiene (HTPB).

HTPB nitromercurates more cleanly than CTBN under non-aqueous phase-transfer conditions. Soluble nitromercurated polymer is obtained as a viscous yellow to brown material which readily redissolves in methylene chloride. Data from selected runs are presented in Table II and important conclusions are given below.

Table II

- 1) Nitromercuration beyond the 25% level gives insoluble polymer.
- 2) Only one equivalent of sodium nitrite is necessary.
- 3) Conditions (run 3, Table II) have been found which produce an excellent yield of 20% nitrated polymer with good selectivity for formation of nitro functionality. This selectivity is apparent in Figure 2.
- 4) Of the 3 types of olefin present in HTPB, the pendant vinyl groups react most rapidly. This is clear from IR data in Figure 2 which shows greatly reduced C-H out of plane bending for terminal vinyl ( $990$  and  $910\text{ cm}^{-1}$ ) in nitromercurated HTPB.
- 5) As is the case for CTBN, soluble nitromercurated polymer is characterized by  $N/Hg > 1$  while the insoluble product has  $N/Hg < 1$ . However, there is no evidence for spontaneous demercuration in the case of HTPB.

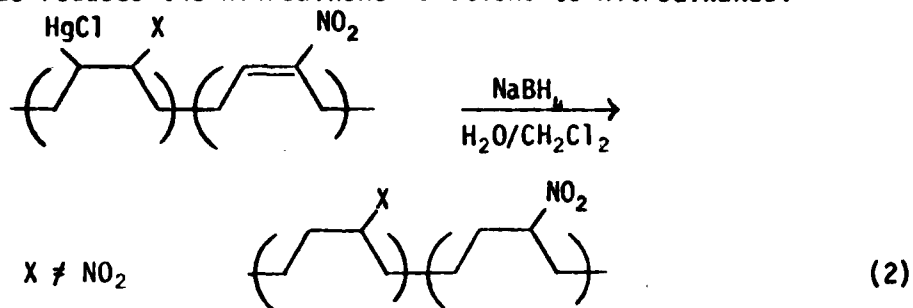
Figure 2

#### C. Demercuration of Nitromercurated Polymers

Studies have been conducted using poly(cis-1,4-butadiene) and HTPB. Survey of a large number of possible conditions has led to the conclusion that 1,5-Diazabicyclo[5.4.0]undecene-5 (DBU) in methylene chloride is the reagent of choice.

Table III      Study of demercuration stoichiometry (Tables III and IV) shows the  
 Table IV      initial increment of base causes some loss of nitro groups as well as demercuration but that subsequent increments of base while causing demercuration  
 Table V      cause no further loss of nitro groups. A kinetic study (Table V) showed that demercuration is rapid, 2 min. being sufficient for completion. Finally, all our experiments revealed that a small fraction, ca. 10%, of the mercury in the nitromercurated polymers was inaccessible to base.

We have shown that sodium borohydride removes this residual mercury rapidly and quantitatively (Cf run 6, Table III). At the same time borohydride reduces the nitroalkene functions to nitroalkanes.



The polymers thus produced are viscous brown liquids which are readily soluble in methylene chloride.

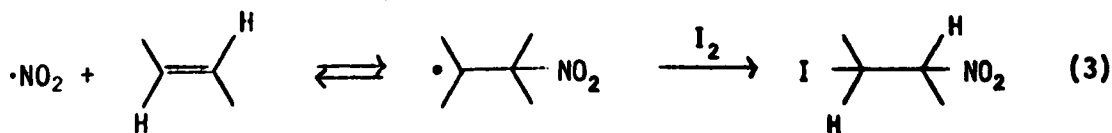
Figure 3

Figure 4

Figure 3 shows the IR spectra of nitromercurated-demercurated and borohydride-treated polybutadiene. Figure 4 shows the IR spectrum of nitromercurated-demercurated HTPB. A sample of HTPB which was nitromercurated, demercurated and finally treated with borohydride has been supplied to Dr. Kurt F. Mueller, Head of the Synthesis and Formulations Branch, Naval Surface Weapons Center, White Oak, Silver Spring, MD.

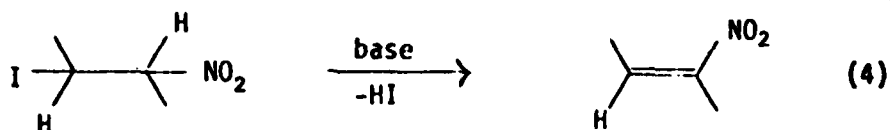
#### D. Iodonitration-Dehydroiodination

Our experiments on reduction of  $\beta$ -nitromercuri compounds reveal that the intermediate  $\beta$ -nitroalkyl radicals lose  $\text{NO}_2$  rapidly to produce olefin. When olefins are treated with  $\text{NO}_2$ , a small equilibrium concentration of  $\beta$ -nitroalkyl radical should be generated. Iodonitration of olefins represents a successful trapping of this radical with iodine.

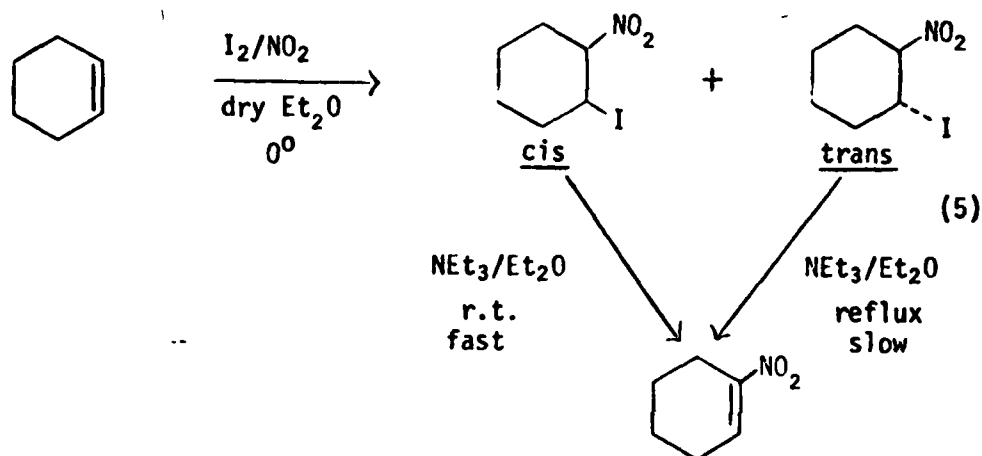




Subsequent dehydroiodination would give nitroolefin.



We have studied this reaction using cyclohexene and 2-hexene as model substrates. The scheme below shows transformations of cyclohexene in diethyl ether.



2-Hexene behaves in a similar fashion though IR indicates that some nitrate ester is formed as a by-product. When the solvent is changed from ethyl ether to  $\text{CH}_2\text{Cl}_2$  or THF, cyclohexene also gives substantial amounts of nitrate ester. Initial reactions with HTPB show that nitrate ester formation also occurs in this case but that cross-linking reactions do not appear to be occurring.

Since easy dehydroiodination is expected on the basis of model studies, the major challenge is to understand the solvent effect and to control it to produce nitro iodide products. We are currently studying this using the

working hypothesis that the solvent effect operates by changing the proportions of the species  $\text{NO}_2$  (source of nitro iodide) and  $\text{N}_2\text{O}_4$  (source of nitrate ester).

## II. Azidation

### A. Cyclohexene.

Reaction of  $\text{NaN}_3$  and  $\text{ICl}$  with cyclohexene follows the procedure of Hassner and Levy<sup>2</sup> but afforded better yields than reported. Furthermore, using  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR, it was shown that the stereochemistry is solvent sensitive. In  $\text{CH}_3\text{CN}$  the reaction is regiospecific to give trans-1-azido-2-iodocyclohexane. In  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  medium some cis product was also produced.

The dehydroiodination reaction was markedly promoted by the use of 18-crown-6-ether which aids in the transfer of  $t\text{-BuO}^-$  into the organic phase. The reaction appears to be completed in 13 hours at  $25^\circ$ , and the mechanism is anti-elimination. The product is 3-azidocyclohexene which is an unstable allyl azide which commences to decompose at  $50^\circ$ .

### B. n-Hexene.

Azidoiodination of n-hexene led to 2-azido-1-iodohexane as the major product and 1-azido-2-iodohexane as the minor product. Dehydroiodination of these compounds occurred even with more ease than that found for azidoiodocyclohexane. The resulting vinyl azides are more stable than the allyl azides; the decomposition begins at  $100^\circ$ .

### C. Polymers.

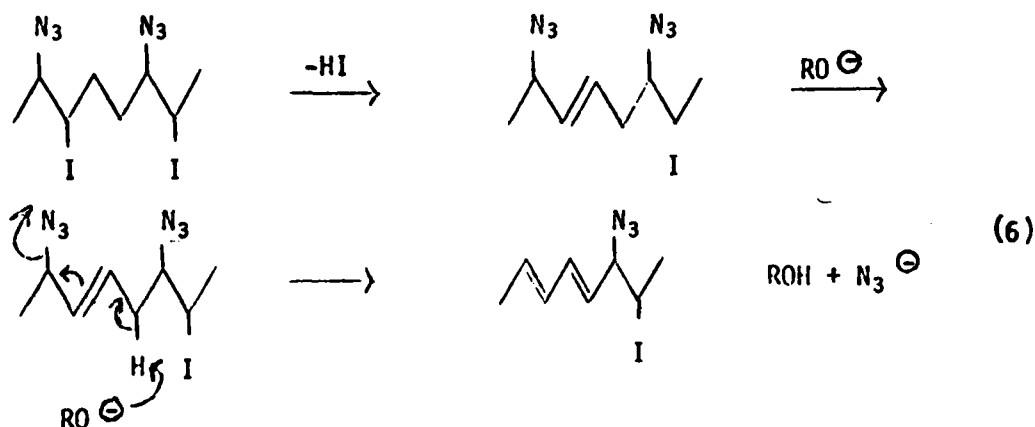
The above reactions were successfully applied to PB, HTPB, and CTBN. A  $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$  solvent mixture is required because of the solubility characteristics of the polymers.

Azidoiodination of the polymers generally resulted in higher yields than the corresponding reactions with the model compounds; the yields increased in the order of  $\text{CTBN} < \text{HTPB} < \text{PB}$ . The results are summarized in

Table VI    Table VI.

Whereas the azidoiodinated polymers are all soluble in the reaction medium, isolation of the  $\text{IN}_3\text{-PB}$  and  $\text{IN}_3\text{-CTBN}$  led to products which cannot be redissolved. The  $\text{IN}_3\text{-HTPB}$  does not suffer from this drawback. Consequently, the azidoiodinated polymers were not usually isolated but dehydroiodination was carried out directly.

The dehydroiodination was catalyzed by  $t\text{-BuOK}$ . It was found that Table VII the optimum condition is using stoichiometric amounts of the base (Table VII). Less than stoichiometric quantity of  $t\text{-BuOK}$  led to incomplete dehydroiodination; an excess causes large loss of nitrogen. It is suspected that the following reaction is responsible for the loss of azide groups.



The azido derivatives of the polymers all have onset of decomposition at  $100^\circ$ .

### III. Significance of This Work

We have demonstrated that water insoluble polymers can react efficiently with aqueous reagents in the presence of phase transfer catalysts and that solid to liquid phase transfer also is effective. Derivatives of binder elastomers currently used by the Navy possessing pendant nitro and azido groups have been produced. Substantial improvements over literature procedures have been devised for several reactions, especially nitromercuration

of olefins. Characterization of the substituted polymers will yield data of great significance for design and characterization of new high energy elastomers.

#### IV. References

1. J.C.W. Chien, T. Kohara, C. P. Lillya, T. Sarubbi, B.-H. Su and R. S. Miller, J. Polym. Sci. Polym. Chem. Ed., 18, 2723 (1980).
2. A. Hassner and L. A. Levy, J. Am. Chem. Soc., 87, 4203 (1965).

#### V. Publication

Phase Transfer-Catalyzed Nitromercuration of Diene Polymers, J.C.W. Chien, T. Kohara, C. P. Lillya, T. Sarubbi, B.-H. Su, and R. S. Miller, J. Polym. Sci. Polym. Chem. Ed., 18, 2723-2729 (1980).

Table I<sup>a</sup> Nitromercuration of Carboxy-Terminated Butadiene-Acrylonitrile Copolymer

Run	Reaction Time (hr.)	Fraction	Weight (g)	% Nitromercuration Based on Total Weight Increase	% Nitromercuration Based on Hg Analysis	N Analysis
1	8	soluble			8.0	13.4
2	16	soluble insoluble	1.31 0.90	17.7	10.1 39.9	17.3 33.2
3	24	soluble insoluble	1.39 1.71	34.2	12.0 42.8	15.9 28.2
4 <sup>b</sup>	24	soluble insoluble	1.40 2.13	41.3	11.4 45.8	16.7 28.5
5 <sup>c</sup>	23	soluble insoluble	3.76 11.38	50.0	- -	- -
6	100	soluble insoluble	0.85 7.80	70.7	20.0 60.3	23.6 36.1

<sup>a</sup>For experimental conditions see Chien et al., *J. Polym. Sci.-Chemistry*, **18**, 2723 (1980).

<sup>b</sup>1.0 mole eq. NaNO<sub>2</sub> used instead of the customary 2.0 mole eq.

<sup>c</sup>Scaled up 5 times and all reagents at 5 times higher concentration than other runs.

Table II Nitromercuration of HTPB

Run	Reagents Used (to 1 eq. of "C=C")	Rxn. Time (Hr.)	Relative Absorbance				Wt. Ratio of Product (insol./sol.)	% Yield by Wt. Gain	Yield by Microanalysis		
			$\frac{A_{1544}}{A_{1445}}$	$\frac{A_{1638}}{A_{1445}}$	$\frac{A_{1638}}{A_{1544}}$	$\frac{A_{1638}}{A_{1544}}$			sol.	Nitrogen	Mercury
1	1 eq. HgCl <sub>2</sub> 2 eq. NaNO <sub>2</sub>	8	sol. 2.83	0.71	0.25		$\frac{0.0116}{2.2026} = 0.0053$	19.87	sol.	17.96	14.20
			insol.						insol.		
2	1 eq. HgCl <sub>2</sub> 2 eq. NaNO <sub>2</sub>	24	sol. 3.73	0.97	0.26		$\frac{1.1211}{1.4129} = 0.7935$	25.72	sol.	22.48	11.74
			insol. 3.99	0.41	0.10				insol.	43.52	44.84
3	1 eq. HgCl <sub>2</sub> 1 eq. NaNO <sub>2</sub>	8	sol. 2.29	0.58	0.25		$\frac{0.0207}{2.5738} = 0.0080$	26.85	sol.	20.16	15.24
			insol.						insol.		
4	1 eq. HgCl <sub>2</sub> 1 eq. NaNO <sub>2</sub>	16	sol. 2.39	0.82	0.34		$\frac{1.3126}{1.6804} = 0.7811$	33.92	sol.	20.36	16.56
			insol. 2.83	0.45	0.16				insol.	33.76	49.32
5	1 eq. HgCl <sub>2</sub> 1 eq. NaNO <sub>2</sub>	24	sol.				$\frac{1.3626}{1.3655} = 1.4372$	39.82	sol.	22.76	15.04
			insol. 4.23	0.52	0.12				insol.	36.32	45.37
6	0.5 eq. HgCl <sub>2</sub> 0.5 eq. NaNO <sub>2</sub>	24	sol. 2.33	0.73	0.31		$\frac{0.0108}{1.9396} = 0.0056$	15.44	sol.	11.68	17.92
			insol.						insol.		

Table III Demercuration of Nitromercurate. Poly(butadiene)

Run	Starting Polymer	Eq. DBU	Products <sup>a</sup>			
			Number	Molecular Formula	% Mercuration	% Nitrogen
b		-	50A	C <sub>4</sub> H <sub>6.6</sub> N <sub>0.34</sub> Hg <sub>0.29</sub>	29	34
1	50A	0.33 <sup>c</sup>	54A	C <sub>4</sub> H <sub>6.0</sub> N <sub>0.19</sub> Hg <sub>0.20</sub>	20	19
2	54A	0.75 <sup>c</sup>	54B	C <sub>4</sub> H <sub>6.1</sub> N <sub>0.18</sub> Hg <sub>0.11</sub>	11	18
3	54B	1.0 <sup>c</sup>	54C	C <sub>4</sub> H <sub>6.2</sub> N <sub>0.16</sub> Hg <sub>0.044</sub>	4.4	16
4	54C	1.25 <sup>c</sup>	54D	C <sub>4</sub> H <sub>6.3</sub> N <sub>0.15</sub>	<u>    </u> <sup>d</sup>	15
5	50A	1.0	55A	C <sub>4</sub> H <sub>6.0</sub> N <sub>0.21</sub> Hg <sub>0.046</sub>	4.6	21
6	53A	XS NaBH <sub>4</sub>	55B	C <sub>4</sub> H <sub>6.4</sub> N <sub>0.19</sub> Hg <sub>0.005</sub>	0.5	19

<sup>a</sup>All reactions 10 min. in CHCl<sub>2</sub> at room temperature.

<sup>b</sup>The analytical figures are for the starting nitromercrated polybutadiene.

<sup>c</sup>Cumulative equivalents DBU sample was exposed to in the course of sequential runs 1-4.

<sup>d</sup>Insufficient sample for Hg analysis. Other runs with XS base have left ca. 5% of the original Hg.

Table IV Demercuration of Hydroxyterminated Poly(butadiene) with DBU

<u>Sample</u>	<u>Equiv. DBU</u>	<u>Elemental Analysis</u>	<u>% Demercuration</u>	<u>% Denitration</u>
TRS-III-68 <sup>a</sup>	-	C <sub>4</sub> H <sub>6.7</sub> N <sub>0.176</sub> Hg <sub>0.196</sub>	-	-
TRS-III-68A <sup>b</sup>	1.0	C <sub>4</sub> H <sub>6.42</sub> N <sub>0.147</sub> Hg <sub>0.0566</sub>	71.1	16
TRS-III-68B <sup>b</sup>	1.35	C <sub>4</sub> H <sub>6.28</sub> N <sub>0.147</sub> Hg <sub>0.0367</sub>	81.3	16
TRS-III-68D <sup>b</sup>	2.0	C <sub>4</sub> H <sub>6.26</sub> N <sub>0.149</sub> Hg <sub>0.0243</sub>	87.6	16

<sup>a</sup>Starting nitromercurated polymer.

<sup>b</sup>All reactions done in CH<sub>2</sub>Cl<sub>2</sub> at room temp. with 2 min. reaction time. Reactions were quenched with 1.2 m HCl and washed with H<sub>2</sub>O and NH<sub>4</sub>Cl (sat.) sol. respectively and CH<sub>2</sub>Cl<sub>2</sub> layer dried over MgSO<sub>4</sub>.



Table V Demercuration of Nitromercurated HTPB with DBU (Time Study)

<u>Sample</u>	<u>Time (Sec)</u>	<u>Elemental Analysis</u>	<u>% Demercuration</u>	<u>% Denitration</u>
TRS-III-72A <sup>a</sup>	-	C <sub>4</sub> H <sub>6.84</sub> N <sub>0.164</sub> Hg <sub>0.151</sub>	0	0
TRS-III-74A <sup>b</sup>	5	C <sub>4</sub> H <sub>6.49</sub> N <sub>0.094</sub> Hg <sub>0.028</sub>	81.5	43.0
TRS-III-74B <sup>b</sup>	15	C <sub>4</sub> H <sub>6.37</sub> N <sub>0.093</sub> Hg <sub>0.021</sub>	86.1	43.3
TRS-III-74C <sup>b</sup>	30	C <sub>4</sub> H <sub>6.73</sub> N <sub>0.123</sub> Hg <sub>0.021</sub>	86.1	25.0
TRS-III-74D <sup>b</sup>	60	C <sub>4</sub> H <sub>6.36</sub> N <sub>0.104</sub> Hg <sub>0.023</sub>	84.8	36.6
TRS-III-73A <sup>b</sup>	120			

<sup>a</sup>Starting nitromercurated polymer.

<sup>b</sup>Same amount DBU used in each reaction.

Each reaction run at room temp. in CH<sub>2</sub>Cl<sub>2</sub>. Reactions were quenched by acidification with HCl (1.2 M) and washed with H<sub>2</sub>O and NH<sub>4</sub>Cl (sat.) sol. respectively and CH<sub>2</sub>Cl<sub>2</sub> was dried over MgSO<sub>4</sub>.

About 2.66 equiv. DBU used in demercurations above.

Table VI Azidoiodination of Butadiene Polymers<sup>a</sup>

Polymer	Run #	[Butadiene]	Solvent CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN	Reaction Time, hrs.	Wt.	Yield, %	
		[IN <sub>3</sub> ]				Iodine	Nitrogen
PB	1A	1.07	4	24	88	88	96
"	18B <sup>a</sup>	"	"	10	b	77	77
"	18B <sup>b</sup>	"	"	"	56	67	82
"	19A	"	5	"	88	88	96
"	23B	0.54	4	24	61	34	21
HTPB	62A	1.07	1	"	82	84	87
"	73A	0.4	1	"	b	40	35
PBAN	33A	1.07	2	25	80	76	76
"	47A	"	"	"	b	76	78
"	33B	0.56	"	"	73	40	30

<sup>a</sup>All reactions performed at 25° C.

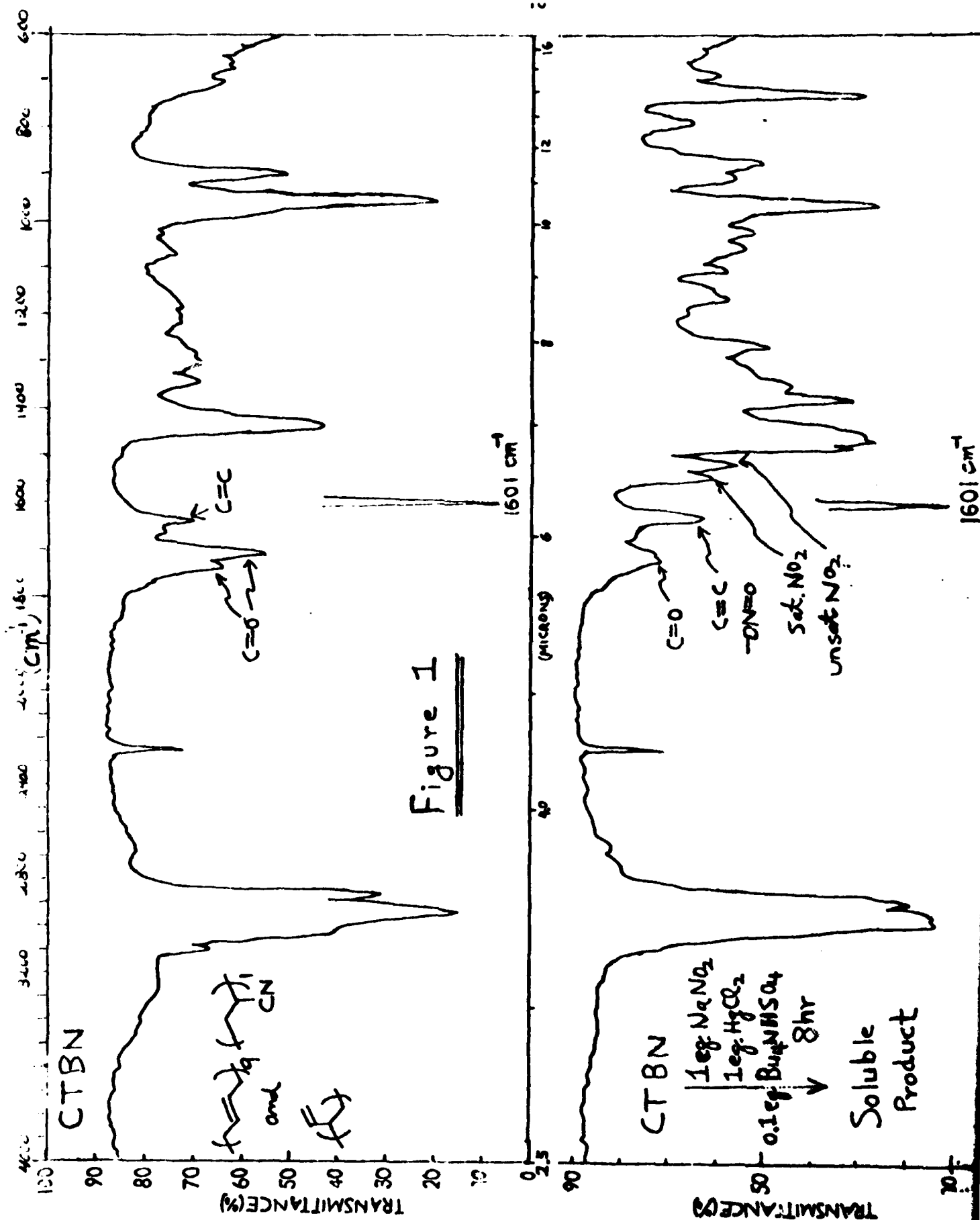
<sup>b</sup>Product was an emulsion.

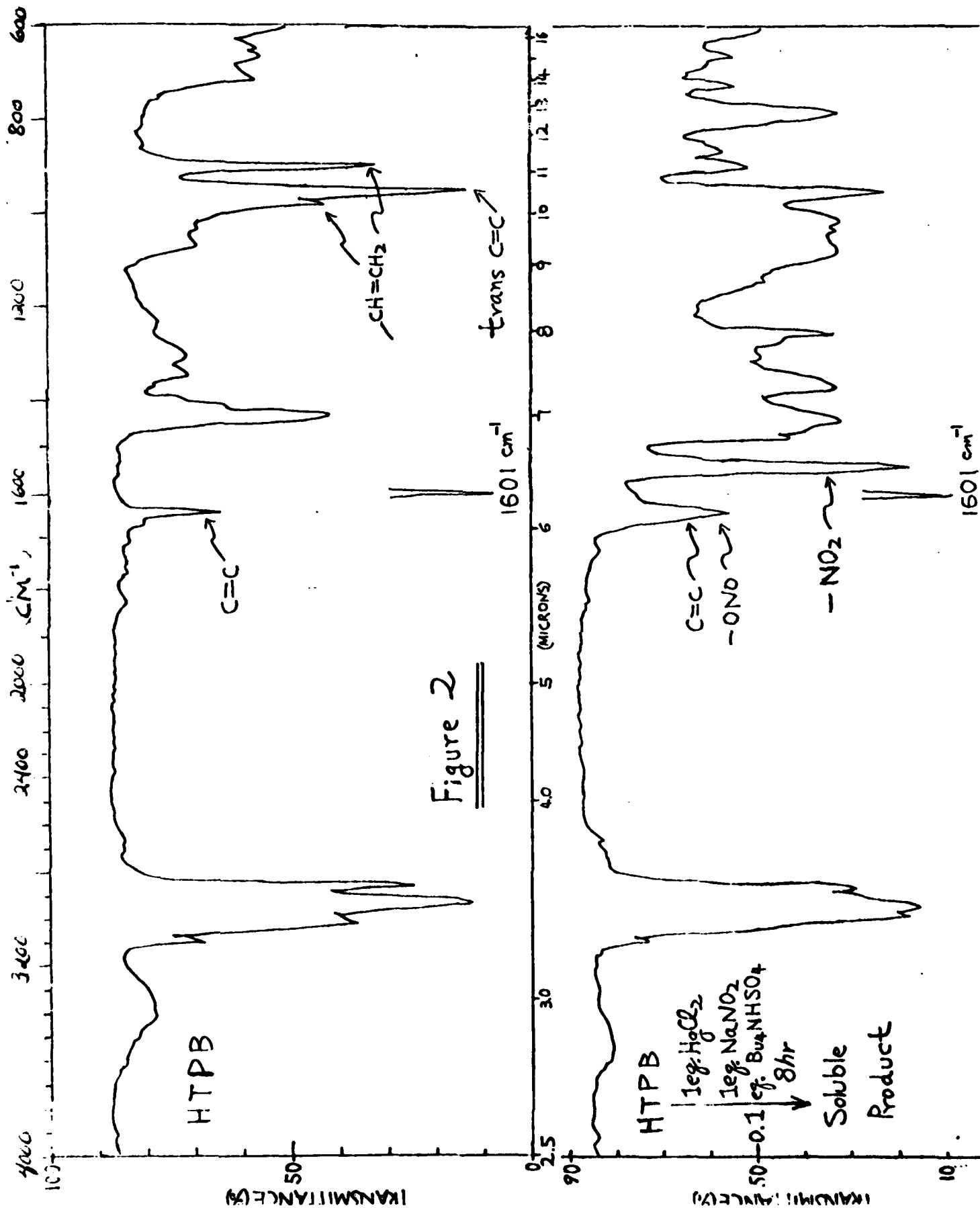
Dried IN<sub>3</sub>-HTPB can be redissolved in THF, DMF, DMSO, and dioxane. These solubility characteristics are independent of whether the products were worked up in the dark or with light.

Table VII Dehydroiodination of Azidoiodinated Butadiene Polymers<sup>a</sup>

Polymer	Run #	<u>t-BuOK</u> Iodine in Polymer	% Iodine in Polymer		% Nitrogen in Polymer	
			Initial	Final	Initial	Final
IN <sub>3</sub> -PB	54A	0.2	88	52	96	63
"	54B	0.4	88	40	96	71
"	54C	0.6	88	21	96	63
"	21F	1.5	88	0.001	96	48
"	30B	"	88	0.1	96	50
"	29A	"	34	0.05	21	22
IN <sub>3</sub> -PBAN	57A	0.2	82	49	88	75
"	57B	0.4	"	30	"	77
"	57C	0.6	"	13	"	75
"	64A	0.8	"	0.1	"	72
"	64B	0.9	"	0.03	"	71
"	64C	0.99	"	0.03	"	68
"	48A	1.0	76	0.14	78	55
"	34A	1.5	"	~ 0	"	45
"	45A	2.0	"	0.015	"	44
"	48B	2.0	"	~ 0	"	46
IN <sub>3</sub> -HTPB	71A	0.8	84	15	87	68
"	71B	0.9	"	8	"	64
"	71C	0.99	"	8	"	63

<sup>a</sup>Reaction conditions: 24 hrs., 25° C, with 5 mole % of 18-crown-6 ether.





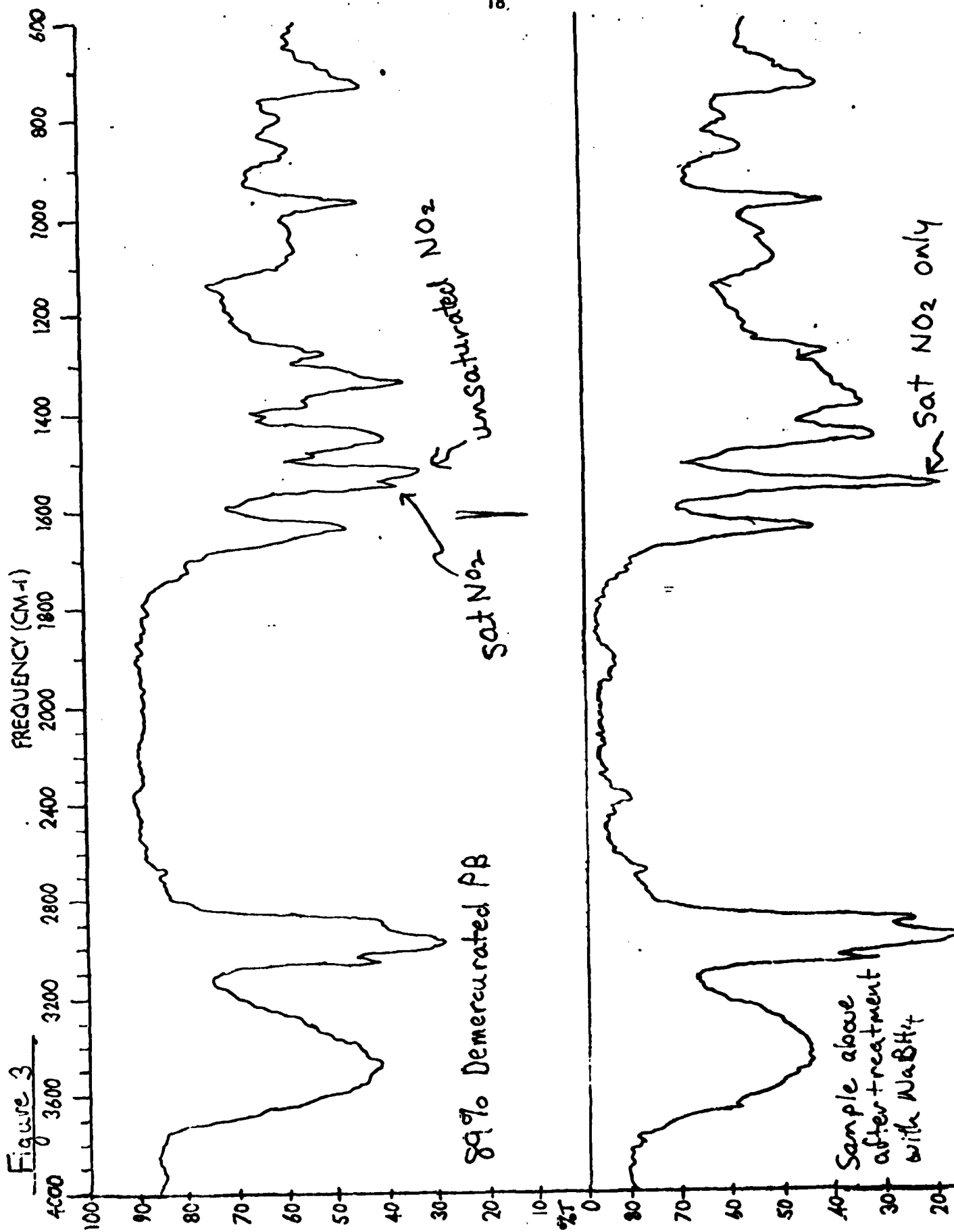
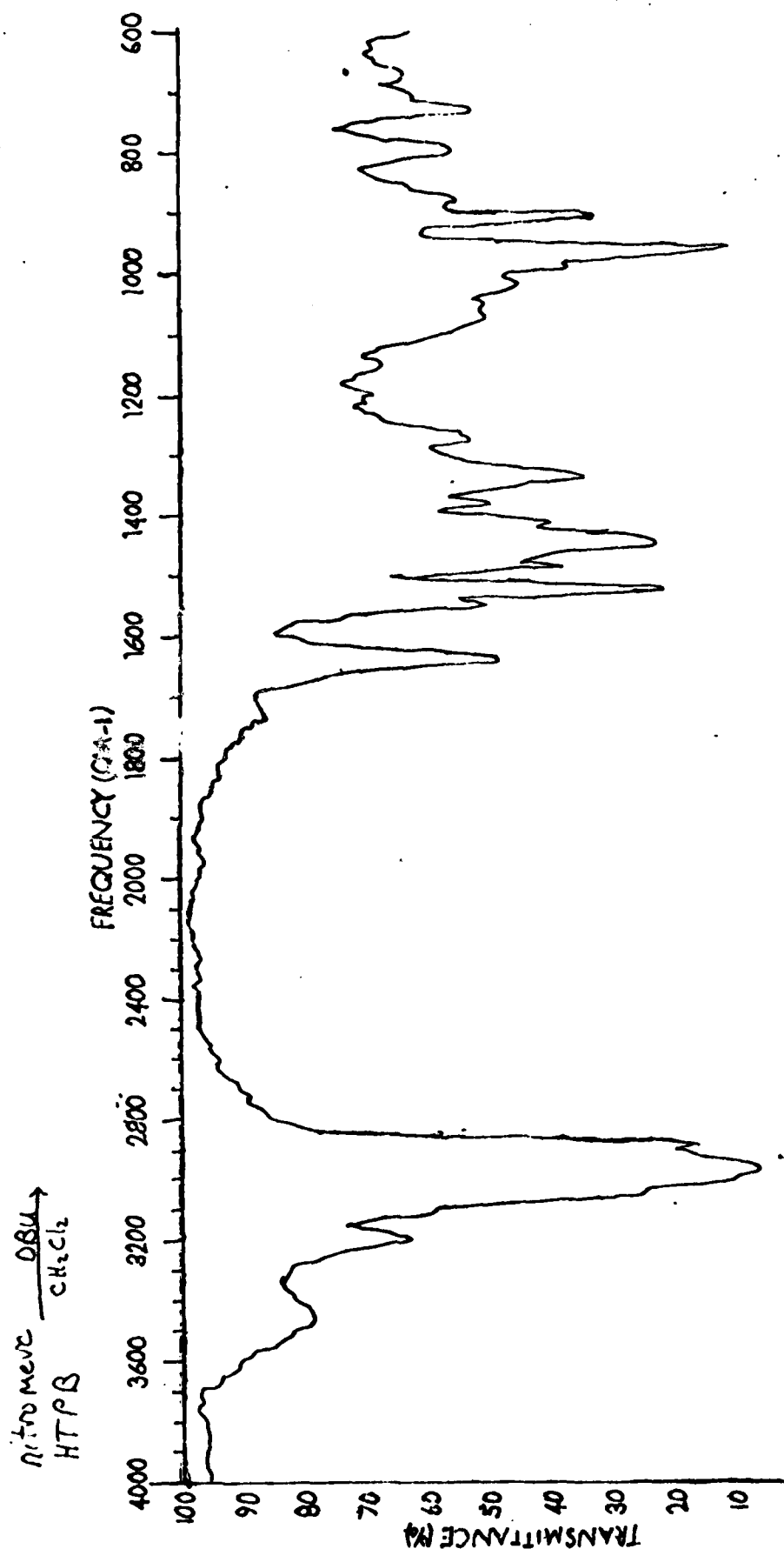


Figure 4



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